

Derivation of generalized Young's Equation for the Wetting Phenomena of Cylindrical Droplets

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Abstract

The contact angles of cylindrical droplets on smooth and chemically homogeneous non-deformable substrates were studied by methods of thermodynamics. The total grand potential of the system was calculated. Then, a generalized Young's equation for wetting of cylindrical droplets on chemically homogeneous and smooth substrates was derived based on the thermodynamic equilibrium condition. The theoretical derivation of the generalized Young's equation is a typical application of Gibbs' theory of capillary phenomena.

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1. Introduction

Wetting phenomena are common in solid-liquid-gas systems, for instance, wetting of liquid droplets on solid surfaces, adhesives, lubricants and capillary penetration in to porous media [1,2]. Wetting abilities are important in many industrial applications, for example, the wetting abilities of electrolytes on electrodes plays a key role in improving the specific energy density of super-capacitors [3] and lithium-ion batteries [4].

In 1805, Thomas Young argued that the contact angle θ for the wetting of spherical droplets on smooth and chemically homogeneous substrates is determined by the following equation [5]

$$\cos \theta = \frac{S_{SG} - S_{SL}}{S_{LG}} \quad (1)$$

Where, s_{LG} is the surface tension of the liquid-vapor interface corresponds to the choice of the surface of tension as a dividing surface, s_{SG} is the surface free energy per unit area of the solid-vapor interface, s_{SL} is the surface free energy per unit area of the solid-liquid interface.

Now, Eq. (1) is called the Young's equation. The Young's equation Eq. (1) is widely applied to macroscopic capillary phenomena [2, 4].

In 1878, Gibbs for the first time gave a theoretical derivation of the Young's equation Eq. (1) based on the theory of thermodynamics [7]. Since then, many theoretical research works have been carried out [2].

However, for cylindrical droplets, the validity of the Young's equation Eq. (1) is still open. The purpose of this paper is to present a theoretical study the contact angles of cylindrical droplets on smooth and chemically heterogeneous substrates by methods of thermodynamics.

2. The Helmholtz free energy for wetting of a cylindrical droplet on smooth substrate

Consider a single-component cylindrical liquid droplet in contact with chemically homogeneous and smooth substrates. The solid surface may be either hydrophobic or hydrophilic. An illustration of hydrophilic wetting is shown in Figure 1.

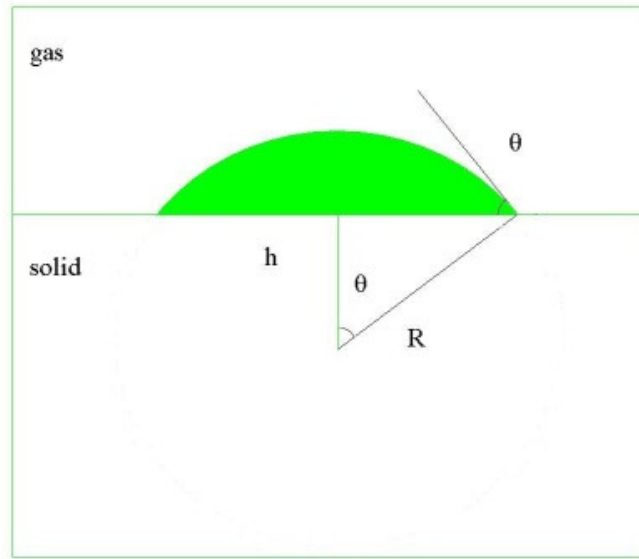


Figure 1. Wetting of a cylindrical droplet on a smooth substrate

For simplicity, we only consider the case of hydrophilic wetting. The same result can be obtained for the case of hydrophobic wetting.

The gradient of density at any point is nonzero in a liquid-vapor transition layers. According to Gibbs[8], we can always choose a set of parallel surfaces which are everywhere perpendicular to the density gradient. Any one of these mathematical surfaces can be chosen to be what Gibbs calls the dividing surface. Detailed discussion of dividing surface can be found in Ref. [8,9,10]. To further investigate this concept, the students or beginners in this field are encouraged to consult Gibbs's original paper [7]. We also attempt to explain this concept in detail in Ref. [11].

Introducing Gibbs's concept of dividing surface and the concept of dividing line [7,9-10], the above solid-liquid-vapor system can be divided into six subsystems, i.e. liquid phase, vapor phase, the liquid-vapor interface, the solid-liquid interface, the solid-vapor interface and the three-phase contact line.

Therefore, the total Helmholtz free energy F of the system is the sum of the Helmholtz free energies of these seven parts. Thus, we have

$$F = F_L + F_G + F_{LG} + F_{SL} + F_{SG} + F_{SLG} \quad (2)$$

Where, F is the total Helmholtz free energy, $F_G, F_L, F_{LG}, F_{SL}, F_{SG}$ and F_{SLG} are the Helmholtz free energies of the seven parts respectively.

The Helmholtz free energies of these seven parts can be written as

$$F_L = -p_L V_L + m_L N_L \quad (3)$$

$$F_G = -p_G V_G + m_G N_G \quad (4)$$

$$F_{LG} = s_{LG} A_{LG} + m_{LG} N_{LG} \quad (5)$$

$$F_{SL} = s_{SL} A_{SL} + m_{SL} N_{SL} \quad (6)$$

$$F_{SG} = s_{SG} A_{SG} + m_{SG} N_{SG} \quad (7)$$

$$F_{SLG} = k L_{SLG} + m_{SLG} N_{SLG} \quad (8)$$

where p_L and p_G are the pressures of the liquid phase and the vapor phase respectively, V_L and V_G are the volumes of the liquid phase and the vapor phase respectively, m is the chemical potential of the six subsystems, $N_L, N_G, N_{LG}, N_{SL}, N_{SG}$ and N_{SLG} are the mole numbers of molecules of the liquid phase, the vapor phase, the liquid-vapor interface, the solid-liquid interface, the solid-vapor interface and the three-phase contact line respectively, A_{LG}, A_{SL} and A_{SG} are the surface area of the liquid-vapor interface, the solid-liquid interface, the solid-vapor interface respectively, s_{LG}, s_{SL} and s_{SG} are the surface tensions of the liquid-vapor interface, the solid-liquid interface, the solid-vapor interface respectively, L_{SLG} is the value of the length of the three-phase contact line, k is the line tension.

In order to calculate the geometrical quantities in the above equations, we may introduce the following assumption:

Assumption 1: Suppose the equilibrium shape of a droplet on a smooth and homogeneous solid substrate is a part of a cylinder which was cut by a plane parallel to the axis of the cylinder.

Now let us calculate some related geometrical quantities in the above equations respectively.

The total volume V_t of the system is

$$V_t = V_L + V_G. \quad (9)$$

The volume of liquid phase V_L is,

$$V_L = (\theta - \sin \theta \cos \theta) R^2 L \quad (10)$$

Where, R is the radius of the cylindrical liquid droplet, θ is the contact angle, L is the length of the cylindrical liquid droplet.

Based on the above relations, we have

$$F_L = -p_L (\theta - \sin \theta \cos \theta) R^2 L + m N_L \quad (11)$$

$$F_G = -p_G [V_t - (\theta - \sin \theta \cos \theta) R^2 L] + m N_G \quad (12)$$

The surface area A_{LG} of the liquid-vapor interface is

$$A_{LG} = 2\theta RL \quad (13)$$

The total surface area A_t of the solid-liquid interface and the solid-gas interface is

$$A_t = A_{SL} + A_{SG}, \quad (14)$$

Where, A_{SG} is surface area of the solid-gas interface, A_{SL} is the surface area of the solid-liquid interface.

The surface area A_{SL} of the solid-liquid interface is

$$A_{SL} = 2R \sin \theta L \quad (15)$$

The length L_{SLG} of the three-phase contact line is

$$L_{SLG} = 2L. \quad (16)$$

Now based on Eq.(13), Eq.(15) and Eq.(16), we have

$$F_{LG} = s_{LG} 2\theta R^2 (1 - \cos \theta) + mN_{LG} \quad (17)$$

$$F_{SL} = s_{SL} (2R \sin \theta L) + mN_{SL} \quad (18)$$

$$F_{SG} = s_{SG} (A_t - 2R \sin \theta L) + mN_{SG} \quad (19)$$

$$F_{SLG} = 2Lk + mN_{SLG}. \quad (20)$$

Therefore, putting Eq. (11-12) and Eq.(17-20) into Eq.(2), the total Helmholtz free energy F can be written as

$$F = -(p_L - p_G) (\theta - \sin \theta \cos \theta) R^2 L - p_G V_t + mN_L + mN_G + s_{LG} 2\theta RL + mN_{SL} + mN_{LG} + (s_{SL} - s_{SG}) 2R \sin \theta L + s_{SG} A_t + mN_{SG} + 2Lk + mN_{SLG} \quad (21)$$

3. Generalized Young's equations based on thermodynamic equilibrium condition

The purpose of this section is to derive a generalized Young's equations for cylindrical droplets on smooth and homogeneous solids by methods of thermodynamics.

According to Gibbs's concept of dividing surface [8], we can choose an arbitrary conformal surface as a dividing surface. Now, we suppose that the radius R of the dividing surface has already been chosen according to some fixed conditions. The contact angle θ now becomes variable.

The thermodynamic equilibrium condition at a fixed temperature T of an open system is [10]

$$\left(\frac{\partial \Omega}{\partial \theta} \right)_{T, \mu} = 0 \quad (22)$$

Where, the subscript T and μ stands for fixed temperature T and fixed chemical potential μ .

It is convenient to introduce the concept of grand potential to treat an open system. The definition of the grand potential Ω of a system is [9]

$$\Omega = \sum_{i=1}^{\tau} (F_i - \mu_i N_i), \quad (23)$$

where τ is the number of subsystems of the system, F_i is the Helmholtz free energy of the i -th subsystem, μ_i is the chemical potential of the i -th subsystem, N_i is the mole numbers of molecule of the i -th subsystem.

Putting Eq. (23) into Eq. (22), the thermodynamic equilibrium condition becomes [10]

$$\left(\frac{\partial \Omega}{\partial \theta} \right)_{T, \mu} = 0. \quad (24)$$

Putting Eq. (11-12) and Eq. (17-19) into Eq. (23), the total grand potential Ω of the above system is,

$$\Omega = (p_L - p_G) (\theta - \sin \theta \cos \theta) R^2 L - p_G V_t + s_{LG} 2\theta RL + (s_{SL} - s_{SG}) 2R \sin \theta L + s_{SG} A_t + 2Lk \quad (25)$$

Putting Eq. (25) into Eq. (24), we have

$$\begin{aligned} & -(p_L - p_G) \left(\frac{\partial f_1}{\partial \theta} \right)_{T,\mu} - f_1 \left(\frac{\partial (p_L - p_G)}{\partial \theta} \right)_{T,\mu} \\ & + s_{LG} \left(\frac{\partial f_2}{\partial \theta} \right)_{T,\mu} + f_2 \left(\frac{\partial \sigma_{LG}}{\partial \theta} \right)_{T,\mu} \\ & + (\sigma_{SG} - \sigma_{SL}) \left(\frac{\partial f_3}{\partial \theta} \right)_{T,\mu} + f_3 \left(\frac{\partial (\sigma_{SG} - \sigma_{SL})}{\partial \theta} \right)_{T,\mu} \\ & + \sigma_{SG} \left(\frac{\partial f_4}{\partial \theta} \right)_{T,\mu} + f_4 \left(\frac{\partial \sigma_{SG}}{\partial \theta} \right)_{T,\mu} \\ & + \kappa \left(\frac{\partial f_5}{\partial \theta} \right)_{T,\mu} + f_5 \left(\frac{\partial \kappa}{\partial \theta} \right)_{T,\mu} = 0, \end{aligned} \quad (26)$$

Where,

$$f_1 = (\theta - \sin \theta \cos \theta) R^2 L \quad (27)$$

$$f_2 = 2\theta RL \quad (28)$$

$$f_3 = 2LR \sin \theta \quad (29)$$

$$f_4 = A_t, \quad (30)$$

$$f_5 = 2L. \quad (31)$$

In order to simplify Eq. (26), we introduce the following assumption.

Assumption 2: Suppose the following equations are valid for the wetting of cylindrical droplets on smooth and chemically homogeneous non-deformable substrates

$$\left(\frac{\partial (p_L - p_G)}{\partial \theta} \right)_{T,\mu} = 0, \quad (32)$$

$$\left(\frac{\partial \sigma_{SL}}{\partial \theta} \right)_{T,\mu} = 0, \quad (33)$$

$$\left(\frac{\partial \sigma_{SG}}{\partial \theta} \right)_{T,\mu} = 0, \quad (34)$$

$$\left(\frac{\partial \sigma_{LG}}{\partial \theta} \right)_{T,\mu} = 0. \quad (35)$$

We have the following results

$$\left(\frac{\partial f_1}{\partial \theta}\right)_{T,\mu} = 2R^2 L \sin^2 \theta, \quad (36)$$

$$\left(\frac{\partial f_2}{\partial \theta}\right)_{T,\mu} = 2RL, \quad (37)$$

$$\left(\frac{\partial f_3}{\partial \theta}\right)_{T,\mu} = 2RL \cos \theta, \quad (38)$$

$$\left(\frac{\partial f_4}{\partial \theta}\right)_{T,\mu} = 0, \quad (39)$$

$$\left(\frac{\partial f_5}{\partial \theta}\right)_{T,\mu} = 0. \quad (40)$$

Putting Eqs. (32-40) into Eq. (26), we obtain,

$$\begin{aligned} & - (p_L - p_G) R \sin^2 \theta + \sigma_{LG} \\ & + (\sigma_{SL} - \sigma_{SG}) \cos \theta + \frac{1}{R} \left(\frac{\partial \kappa}{\partial \theta} \right)_{T,\mu} = 0. \end{aligned} \quad (41)$$

It is known that a generalized Laplace's equation of a free cylindrical droplet in vapor can be written as [12],

$$p_L - p_G = \frac{\sigma_{LG}}{R} + \left[\frac{d\sigma_{LG}}{dR} \right], \quad (42)$$

where the differential in square bracket $\left[\right]$ denotes the change resulted from a mathematical variation of the position of this dividing surface by the amount dR in the same physical system under the same fixed physical state.

Applying Eq. (42), Eq. (41) becomes

$$\begin{aligned} \cos \theta = & \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} + \frac{R \sin \theta \tan \theta}{\sigma_{LG}} \left[\frac{d\sigma_{LG}}{dR} \right] \\ & - \frac{1}{\sigma_{LG} R \cos \theta} \left(\frac{\partial \kappa}{\partial \theta} \right)_{T,\mu}. \end{aligned} \quad (43)$$

Eq. (43) is a generalized Young's equation for wetting of a cylindrical droplet on chemically homogeneous and smooth non-deformable substrates. Eq.(43) is the main results of this work.

Following Gibbs [8, 10], we introduce the concept of surface of tension M_s as follows

$$\left[\frac{d\sigma_{LG}}{dR} \right]_{R=R_s} = 0, \quad (44)$$

where R_s is the radius of the surface of tension M_s .

If we choose the surface of tension M_s as the dividing surface, then Eq. (43) becomes

$$\cos \theta = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} - \frac{1}{\sigma_{LG} R \cos \theta} \left(\frac{\partial \kappa}{\partial \theta} \right)_{T,\mu}. \quad (45)$$

Eq. (45) is a useful generalization of the Young's equations Eq. (1) for wetting of cylindrical droplets.

4. Conclusion:

For wetting of cylindrical droplets on solid surfaces, theoretical verification of the validity of the Young's equation is still open. The contact angles of cylindrical droplets on smooth and chemically homogeneous non-deformable substrates were studied by methods of thermodynamics. The total grand potential of the system was calculated. A generalized Young's equation for wetting of cylindrical droplets on chemically homogeneous and smooth non-deformable substrates was derived based on the thermodynamic equilibrium conditions. The theoretical derivation of the generalized Young's equation is a typical application of Gibbs' theory of capillary phenomena.

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